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(54) Title: METHOD OF RECOVERING ENERGY FROM WASTE LIQUORS FROM PULP PROCESSES

(57) Abstract

Method of recovering energy from waste liquors from pulp processes, wherein the waste liquor is burned in a waste liquor recovery boiler and energy is recovered from the flue gases, which are formed by producing saturated or partially superheated steam in the recovery boiler. According to the invention, a portion of the waste liquor is pressure heat treated to release gases and/or treated in a liquid phase in a pressurized process for converting the waste liquor into a fraction containing an oleaginous fuel and a fraction containing inorganic components. The waste liquor is thereby treated for instance in a hydrogenation process. The waste liquor from the pressure heat treatment and/or the waste liquor fraction containing inorganic components is burned in the recovery boiler. The released gases and/or the fraction containing oleaginous fuel is burned in a separate superheating boiler, in which the steam produced in the recovery boiler is superheated.

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METHOD OF RECOVERING ENERGY FROM WASTE LIQUORS FROM PULP PROCESSES

The present invention relates to a method of recovering  
5 energy from waste liquors from pulp processes. The invention  
relates especially to a method wherein waste liquor is  
burned in a waste liquor recovery boiler, e.g. in a soda  
recovery boiler, and wherein heat is recovered from the  
resulting flue gases by producing saturated and/or partially  
10 superheated steam in the recovery boiler.

When combusting waste liquors in pulp processes, the aim  
is to separate the organic and the inorganic parts of the  
dry substance of the waste liquor from each other. The  
15 heat from the organic part of the dry substance is recovered  
and the largest possible amount of steam is produced by  
means of this heat. Pulping chemicals are recovered from  
the inorganic part of the dry substance in such a form  
that they can, in subsequent stages of processing, be  
20 converted into a suitable form to be reused in the cooking  
process.

The soda recovery boiler has, until now, proved to be  
superior for the recovery of heat and chemicals from waste  
25 liquors. The waste liquor is sprayed in the form of small  
drops into the boiler. In the hot combustion chamber water  
vapor, volatile parts of the dry substance, and eventually  
gasifiable parts of the dry substance evaporate from the  
drops. The gases inflame, thereby delivering heat to the  
30 heat surfaces disposed in the boiler and are discharged from  
the upper end of the boiler. The ash from the waste liquor  
drops, i.e. the inorganic substances of the waste liquor,  
accumulate on the bottom of the boiler, from which they  
are removed and through various stages of processing are  
35 conveyed back to the cooking process.

The flue gases from the soda recovery boiler contain a great deal of ash, e.g. sodium sulfate, a portion of which flows along with the flue gases upwards in the boiler in the form of fine dust or molten drops. The salts contained  
5 in the ash melt at a relatively low temperature and become, when melting, easily adhesive and corrosive. The deposits formed by the molten ash cause the risk of clogging of the flue gas channels and, furthermore, cause corrosion and erosion of the heat surfaces of the boiler. The risk of  
10 clogging and corrosion increases considerably the number of the shutdowns for inspection and maintenance.

A high temperature of the boiler tubes speeds up the formation of deposits and thereby the corrosion of the  
15 heat surfaces. Thus, the deposits affect particularly the heat surfaces for the superheated steam. Usually the corrosion of the materials is reduced by controlling the temperature of the superheater surfaces.

20 In such places in the superheater, in which the temperature tends to rise especially high or in which there is a great deal of liquid-phase chemicals, in other words, where the corrosion and the erosion is a problem, special-alloy steels have to be used. However, even the special-alloy  
25 steels have their maximum operating temperatures, above which they behave in the same way as the cheaper pressure vessel steels. This temperature is substantially lower in soda recovery boilers than in, for instance, oil-fired  
. boilers.

30 The principal way of avoiding corrosion is, anyhow at the present time, to choose a sufficiently low temperature and pressure for the produced steam, whereby the detrimental effects of the molten salt decrease. This means that the  
35 steam cannot be superheated to as high a temperature as desired for the production of electric power in steam turbine plants.

In a steam power plant, the higher the pressure and the temperature of the steam can be raised in the boiler the higher the overall electrical efficiency, i.e. the ratio between the net production of electric power and the consumption of process heat. There is a need to raise the overall electrical efficiency of the soda recovery boilers nearer to that of the conventional coal-fired power plants, i.e., the pressure and the temperature of the steam produced by the soda recovery boilers should be raised to as high a level as possible.

In other industrial boilers, a conventional steam pressure/temperature is, e.g., 130 bar/535 °C. In the soda recovery boilers, the pressure and the temperature have to be regulated in accordance with the strength of the available pressure vessel steels. In the superheater of the soda recovery boilers, ferritic heat resistant steels and austenitic steels reach a longer working life in the hottest part only when the surface temperature of the tubes does not exceed 550 - 600 °C. The temperature of the superheated steam in the soda recovery boilers is therefore usually not allowed to rise to 500 °C. At a pressure of 60 - 90 bar, a temperature of 450 - 480 °C is usually considered to be the maximum temperature.

Attempts have been made to reach higher temperatures than mentioned above, by controlling the combustion process in the boiler. The incoming secondary and tertiary air of the boiler have been controlled in order to achieve as even a combustion process as possible, in which no great temperature variations in the flue gas flow occur. The purpose has been in this way to eliminate sudden and, as regards corrosion, dangerously high temperature peaks in the superheater section, in which case it would be possible to increase the mean temperature in the superheater. In this way, an increase of a few degrees can possibly be achieved in the superheater section temperature.

Attempts have also been made to achieve higher steam temperatures without the risk of corrosion by reducing the fouling of the superheater surfaces. It is possible to some extent, for instance by appropriate feeding of 5 the air, to reduce the amount of molten, inorganic material which is carried by the flue gas flow upwards to the superheater section and which fouls the surfaces of the superheater. On the other hand, the formation of deposits can also be reduced by continuos sweeping.

10 Attempts have also been made to reduce the fouling of the surfaces and the clogging of the flue gas channels by dimensioning the convection section sufficiently large and increasing the distance between the superheater surfaces. 15 Larger clearances facilitate the sweeping and cleaning of the surfaces. These arrangements increase, however, the size of the boiler and are thus, as regards the building costs, unfavourable.

20 A soda recovery boiler in which the size of the superheater has had to be increased is, as regards the heat transfer and evaporation efficiency, inferior to a corresponding coal-fired boiler. The tendency of the superheater surfaces to foul multiplies the number of heat surfaces needed in 25 comparison with a boiler, the flue gases of which contain only small amounts or no ash at all.

The suggested improvements mentioned above have not proved 30 to guarantee a continuos production of steam having a temperature of above 500 °C. The corrosion of the surfaces of the superheater proceeds, in spite of the alterations, at an uneconomically fast rate. So far, no such method is being used in the pulp mills, by means of which steam of the same high quality could be produced in soda recovery 35 boiler plants as in other, conventional power boiler plants.

The object of the present invention is to provide a method which is better than the methods mentioned above for

producing high-quality superheated steam in a process for the recovery of chemicals from the pulp cooking.

5 The object of the invention is in particular to provide a method better than the above mentioned for producing electric energy in a waste liquor burning process.

Thus, the object of the invention is to provide a method by means of which it is possible to significantly reduce 10 the corrosion of the superheater in a waste liquor burning process, whereby a saving in material costs is achieved, but above all the utilization factor of the pulp mill is improved, i.e., the number of shutdowns for service is reduced.

15

The above mentioned objects of the invention are realized by a method, characterized in that

- at least a portion of the waste liquor is treated, before it is conveyed to the recovery boiler, by a pressure 20 heating process, in order to form a gaseous fuel containing organic components, and/or by a pressurized liquid-phase process in order to form a fraction containing an oleaginous fuel and a fraction containing inorganic components;

- the waste liquor from the pressure heating process 25 and/or the fraction containing inorganic components formed by said pressurized liquid-phase process are burned in the recovery boiler, and

- the gas formed during said pressure heating process and/or the fraction containing an oleaginous fuel formed by 30 said pressurized liquid-phase process are burned in the superheating boiler, in which the steam produced in the recovery boiler is superheated.

The invention provides a method for generating steam in a 35 substantially conventional recovery boiler and superheating the steam in a separate superheating boiler by burning gas or oleaginous fuel which is clean of impurities, in-

organic compounds, causing problems at higher temperatures in the recovery boiler.

A separate superheating boiler is known as such. The  
5 improvement according to the present invention is that the same fuel which is used in the recovery boiler, i.e. the waste liquor, may be processed to provide the fuel for the superheating boiler. The waste liquor is pressure heated to give fuel gas or treated by a pressurized liquid-phase process to give an oleaginous fuel. The recovery process  
10 can be performed without auxiliary fuel, such as natural gas or mineral oil.

The pressure heating process or the thermal treatment of  
15 the waste liquor can be arranged to take place between some of the evaporation stages or immediately before the burning. In the pressure heating, the temperature of the waste liquor is raised to a temperature higher than the cooking temperature, preferably to 170 - 350 °C, in order  
20 to split its macromolecular lignine fractions. The heating can be effected by any economically suitable method: direct or indirect steam heating, or some other heating, such as electrical heating. As the source of heat for the pressure heating, for instance bled steam from a steam turbine plant can be used. The treatment time is 10 to 30 min,  
25 typically about 20 min in order to generate a gas that contains a significant amount of organic sulfur compounds. In the pressure heating of black liquor, generally about 1 to 3 weight-% of the dry solids contained therein will be  
30 released as a gas containing dimethylsulfide (DMS).

The gas released during the pressure heating can be used as such as fuel in the superheating boiler. The gas released can be further converted to give methane and hydrogen sulfide, which both could be used separately or together as fuel in the superheating boiler. A gas achieved from black liquor by pressure heating or a subsequent converting to methane and hydrogen sulfide does not contain the

inorganic components of black liquor. The thermal energy of the gas corresponds to that of the pure components. The gas can be burnt as natural gas. If preferred, only the methane may be burnt in the superheating boiler and the 5 hydrogen sulfide may be used to increase the sulfidity of the recovered cooking chemicals.

The total amount of dry solids to be burned in the recovery boiler is decreased if a portion of the organic material 10 is separated in a gaseous form in the pressure heating stage and burned separately. This leads to a decreased load of the recovery boiler or an increase in the capacity of the recovery boiler.

15 By means of the pressure heating, the viscosity of the waste liquor is reduced, which improves the properties of the waste liquor as regards handling and evaporating and transferring it from one stage to another. Thus, the pressure heating renders it possible to evaporate the 20 waste liquor to a very high dry solids content, and for that reason the effective heat value of the waste liquor rises and consequently also the efficiency of the electric power production of the turbine power plant increases.

25 The waste liquor substantially maintains its thermal value after the pressure heating and can, when evaporated to its final dry-solids content, be introduced into the recovery boiler for burning.

30 The pressurized liquid-phase process for the fractionation of the waste liquor is preferably a hydrogenation process, in which a portion of the waste liquor is fractionated into an oil fraction and an inorganic fraction containing the major portion of the inorganic components of the waste 35 liquor before it is conveyed to the recovery boiler. The fractionation is carried out by means of a high pressure and a high temperature under reducing conditions, for instance in the presence of hydrogen or carbon monoxide.

he inorganic fraction formed in this way by the hydrogenation process is burned in the waste liquor recovery boiler, and the oil fraction is burned in the superheating boiler, in which the steam produced in the recovery boiler is  
5 superheated.

In a preferred embodiment of the invention, about 10 - 35 % of the waste liquor is conveyed to the hydrogenation process for fractionation. The main part, about 65 - 90 %  
10 of the waste liquor is conveyed to the recovery boiler without being fractionated. The waste liquor is preferably concentrated to a dry solids content of about 15 - 80 %, most preferably to 30 - 50 % prior to the hydrogenation process. The waste liquor may also be pressure-heated  
15 prior to the hydrogenation process.

In the superheating boiler, superheated steam of > 100 bar and > 520 °C can be produced by the method according to the invention. In the recovery boiler, saturated or  
20 partially superheated steam, for instance steam of < 350 °C can be produced, which is finally superheated in the superheating boiler. The superheating boiler can, if so desired, be pressurized, in which case the space required for it is significantly smaller than that of a conventional boiler. The flue gases from the recovery boiler and the  
25 superheating boiler can be combined and can, for instance, be used for preheating the air required for the combustion process. The flue gases from the superheating boiler can, for instance, be conveyed to the lower part of the recovery  
30 boiler.

The total efficiency of the boiler plant depends, as previously stated, on the pressure and the temperature of the superheated steam, being the higher the higher the values in question are. Taking into consideration the  
35 overall economy, it is advantageous to produce as much electric power as possible with the turbine, whose power

production efficiency increases when the pressure and the temperature increase.

Thus, the spirit of the invention is to produce in a conventional waste liquor recovery boiler, for instance in a recovery boiler resembling the present-day soda recovery boiler, steam of lower quality and to superheat this steam in a separate superheating boiler. The superheating is brought about by flue gases which do not contain appreciable amounts of the corroding impurities present in the flue gases from the soda recovery boiler. The fuel used by the separate superheating boiler is made by a pressure heating or hydrogenation process from the waste liquor, the main part of which is burned in the recovery boiler. Additional fuel, mineral oil or the like, is not essentially needed in the separate superheating, unless it is profitable to use some, owing to the dimensioning or for other reasons.

The waste liquor from a pulp cooking, e.g. black liquor, is concentrated by evaporation before it is burned in the waste liquor recovery boiler. According to the latest technique available, it is possible to concentrate the black liquor up to a dry solids content of 80 %, in which case it is a relatively good fuel. The viscosity of the black liquor has until now imposed a limit to the concentration. By means of a pressure heating process which has been developed, it is possible to reduce the viscosity of the black liquor by heating it under pressure, in which case the evaporation can be carried out up to a very high dry solids content, facilitating thus the burning of the black liquor in a recovery boiler.

The waste liquor can be conveyed from various stages of the evaporation to the hydrogenation according to the present invention, prior to or after pressure heating.

The hydrogenation process is known per se from the Finnish patent specification FI 70057. In the hydrogenation process,

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the black liquor is subjected to a treatment by a reducing agent, such as CO or H<sub>2</sub>, at an elevated pressure and temperature. The treatment results in the formation of an oleous phase, which is insoluble in the aqueous phase and 5 which can easily be separated by decantation. In the process, most of the organic materials are converted into oil, while a small part of them gasifies. The amount of organic material remaining in the aqueous phase is relatively small.

10

In the hydrogenation process, a portion of the waste liquor coming directly from the digester or via the evaporation units or the pressure heater is thus brought into contact with carbon monoxide, hydrogen or some other reducing 15 agent at an elevated pressure and temperature, until substantially all of the organic matter has been converted into liquid or gaseous products. The liquefied part forms a liquid phase, which is insoluble in the aqueous phase, from which it can easily be separated. A pretreatment of 20 the waste liquor is not necessary in the process but can be performed. The hydrogenation is carried out at a pressure of 50 - 200 bar, preferably 100 - 200 bar and a temperature of 200 - 350 °C. In practice all kinds of waste liquor from the pulp industry can be treated by hydrogenation. The 25 reactions can be carried out in reactors of any kind in which a liquid can be treated at an elevated pressure and temperature. The hydrogenation can be performed in one stage or, if desired, in two or a plurality of stages.

30 From waste liquor is thus by hydrogenation produced, by means of a high pressure and a high temperature under reducing conditions, an oleous fraction resembling mineral oil which does not contain appreciable amounts of the inorganic components of the waste liquor and the heat 35 value of which is of the same order as that of mineral oil. It is combusted in the same way as heavy fuel oil.

In the hydrogenation process, the heat value of the fraction containing the inorganic compounds of the waste liquor decreases somewhat as does also its combustability. Therefore, preferably only a portion, preferably less than 5 35 %, of the waste liquor coming from the digester is hydrogenated, in which case the amount of the untreated waste liquor is still large enough for combusting the difficult to burn, inorganic fraction remaining after the hydrogenation, for the recovery of the inorganic salts in 10 it. The inorganic fraction contains inter alia the following sodium salts: NaHS, NaHCO<sub>3</sub>, aliphatic sodium salts, such as sodium acetate and formate, and smaller amounts of other organic salts, which can not be directly returned to the pulp cooking.

15 The oleaginous fraction of the black liquor obtained by hydrogenation can at least partially be used to replace mineral oil required for the pulping process, in which case the self-sufficiency of the pulping process as regards 20 fuel increases. Now it has, surprisingly, been discovered that energy can be recovered from waste liquor from a pulping process at an overall efficiency better than ever before by superheating the steam obtained from a conventional waste liquor recovery boiler in a superheating 25 boiler, in which an oil fraction made from waste liquor by hydrogenation is burned.

The limiting value of the amount of waste liquor which is to be hydrogenated can be calculated from the effective 30 heat value of the inorganic fraction obtained by hydrogenation. Preferably, the inorganic fraction is burned in the recovery boiler by means of the waste liquor without any auxiliary fuel.

35 It is thus a distinguishing feature of the present invention that the waste liquor is pressure heated for releasing organic gases or fractionated into two parts, one of which is oil and the other waste liquor containing the inorganic

components of the waste liquor. The gases or oleous fraction thus received are burned separately in a superheating boiler, in which case the design and the materials of the superheater can be chosen as in any oil-fired boiler without 5 having to consider the harmful effects of the inorganic, molten salts, i.e:

- the superheating surfaces can be spaced much closer to each other than in a soda recovery boiler, because they do not foul to the same extent as in the soda recovery 10 boiler;
- very little or no cleaning at all of the superheating surfaces is needed, because the superheating is effected by clean flue gases;
- the materials for the superheating and other surfaces 15 can be chosen merely on the basis of their heat strength, without having to consider the corrosion risk;
- if it seems desirable from an economical point of view, gases from the pressure heating of waste liquor or oil made from the waste liquor and conventional mineral oil 20 can easily be burned at the same time in the separate superheating boiler, or even mixed together.

The soda recovery boiler or a corresponding waste liquor recovery boiler is still needed for burning the major 25 portion of the waste liquor or black liquor stream and for recovering chemicals. The soda recovery boiler functions, however, in the embodiment according to the invention principally as a vaporizing boiler, in which only a partial superheating is effected at the most. In 30 the vaporizing boiler, the surface temperature of the materials does not rise as high as in the superheating section, wherefore the risk of corrosion is smaller. The superheater possibly disposed in the soda recovery boiler will be small compared with a traditional boiler, as the 35 main part of the superheating is effected in a separate boiler in a considerably hotter environment. The heat surfaces of the superheating boiler are more efficiently used than in a traditional soda recovery boiler, which

means that a smaller amount of tubes are needed in a smaller boiler, in other words: a saving of capital costs is achieved.

5     The flue gases from the separate superheating boiler can be conducted into the flue gases from the soda recovery boiler at some suitable point, in which case their heat content is recovered more efficiently. Their heat can be recovered for instance in the preheating of air as in  
10    conventional power plant boilers. In a traditional soda recovery boiler, the flue gases are too impure to be conducted to the air preheater. By using flue gases for the preheating of air, back-pressure and bled steam can be saved for other purposes.

15

Depending on the required steam and power of the mill, the superheating can be adjusted to some extent, but the steam turbines have an optimum operation point, from which it is not advisable to deviate too much.

20

The pressure and temperature of the separate superheating boiler can be chosen relatively freely so as to suit the steam system of the mill. There is then no need to build separate pipe systems for many different pressures. The  
25    same turbine is available for the steam of the whole mill.

30    The separate superheating boiler and the waste liquor recovery boiler can be built in such a way that their pressure frames are closely connected to each other, for instance by some kind of precombustion chamber construction.

By means of the invention, the following additional advantages can be achieved:

35    - by increasing the pressure and the operating temperature of the steam recovered from the waste liquor recovery process by means of the superheating boiler, the overall electrical efficiency of the plant is improved, i.e. more power is generated by the heat recovered in the steam;

- the design of the recovery boiler will be simpler, since the superheater can be omitted from the upper part of the combustion chamber and the boiler can for that reason be built in the shape of a tower, in which the height of the economizer determines the height of the boiler;
  - 5 - special-alloy steels are either not needed at all with clean flue gases or at least they are required less extensively than in conventional soda recovery boilers, even when operating at higher temperatures;
  - 10 - when burning gases or the oil fraction, substantially no detrimental, melting salt compounds are formed, and for that reason there is significantly less corrosion, even if the boiler is operated at a considerably higher temperature level than at present;
  - 15 - the gases or the oil fraction can be used as starting fuel in the waste liquor recovery boiler, in which case no purchased oil is required for the burning of the waste liquor.
- 20 The invention will now be described more in detail with reference to the accompanying drawing, in which one embodiment of the process for recovery of energy from waste liquor according to the invention is illustrated schematically.
- 25 The unit for recovery of energy from waste liquor shown in the figure comprises evaporator sections 10 and 12, a pressure heating unit 14, a hydrogenation unit 16, a waste liquor recovery boiler 18, a heat recovery section 20 connected to it, a separate superheating boiler 22, an air preheater 24, a steam turbine 26 and a generator 28.
- 30 In the method according to the invention, the pulp coming from the digester house is transferred to the washing department 30, in which the pulp is cleaned and separated from the waste liquor. The waste liquor from the washing, which usually contains about 15 - 20 % dry matter, is led through a line 32 to the first evaporator section 10, in

which the waste liquor is concentrated to a dry solids content of about 45 %. From the first evaporator section the waste liquor is led to the pressure heating unit 14 through a line 34.

5

Gases released during the pressure heating are led through a conduit 35 from the pressure heating unit 14 to the superheating boiler 22.

- 10 From the pressure heating, the waste liquor is led through a line 36 to the evaporator section 12, in which the waste liquor is finally evaporated to a dry solids content of about 80 %. From the final evaporation, the waste liquor is led through a line 38 to be sprayed by nozzles 40 into  
15 the recovery boiler 18.

Combustion air is supplied to the recovery boiler through a line 42 from the air preheater 24. Through the char bed 44 accumulated on the bottom of the recovery boiler, the  
20 molten, inorganic matter flows through an outlet 46 to a dissolving vat, not shown in the figure.

In the recovery boiler 18 and the heat recovery section 20, heat is recovered by means of vaporizing surfaces 48  
25 and a water preheater 50. The flue gases are discharged from the boiler through a line 52. The steam can, if desired, be partially heated in the recovery boiler by means of superheating surfaces 51.

30 To the hydrogenation stage 16 according to the invention can be supplied unevaporated waste liquor through a line 54 or pre-evaporated waste liquor through a line 56 or pre-evaporated and pressure heated waste liquor through a line 58 or, finally, evaporated waste liquor through a  
35 line 60. The oil fraction formed in the hydrogenation stage is led through a line 62 to the superheating boiler 22, and the residual, inorganic fraction is led through a line 64 to be combined, at a desired point, for instance

before the final evaporation, with the waste liquor stream which is to be introduced into the recovery boiler. The small amount of gas which is formed in the hydrogenation stage is removed through a line 66.

5      Combustion air is supplied to the superheating boiler through a line 68 from the air preheater. Superheating surfaces 72 are disposed in the superheating boiler for the superheating of the steam coming from the recovery 10     boiler through steam pipes 74. The superheated steam is led through a line 76 to the steam turbine plant, in which electric power is generated by the turbine 26 and the generator 28.

15     The flue gases are passed from the superheating boiler directly to the upper part of the recovery boiler or through a line 78 to the lower part of the recovery boiler. A portion of the flue gases are passed through a line 80 to the air preheater 24.

20     In the embodiment of the invention described above both gaseous and oleaginous fuel for the superheating boiler are provided for by both pressure heating and hydrogenation of the waste liquor. It is of course possible and may even be 25     more preferable to only use one of the waste liquor treatment processes, either the pressure heat treatment providing a gaseous fuel or the pressure liquid-phase treatment providing an oleaginous fuel.

30     One of the principal starting points when using the pressure liquid-phase treatment is that an appropriate amount of waste liquor, such as black liquor, is fractionated to oil and an inorganic waste liquor residue. By an appropriate amount is meant an amount of waste liquor by the oil 35     fraction of which the desired separate superheating can be accomplished and the inorganic residue fraction of which, when combined with the waste liquor, can be burned in the

recovery boiler essentially without auxiliary fuel in connection with the burning of waste liquor.

By means of the recovery boiler and superheating boiler system, the measures for restricting the pressure and the temperature of the soda recovery boiler are not needed. Thus, the method according to the invention significantly improves the recovery of energy from waste liquor.

The economical profit from the method according to the invention results especially from the big electric power portion in comparison with the steam portion which can be achieved by it. In present-day integrated paper and pulp mills, the steam demand has decreased. Therefore, it is not any more profitable to recover the energy received from the burning of waste liquor in the form of surplus steam but the energy should be recovered in the form of electric power. By means of the system according to the invention, the electric power yield achieved in the paper and pulp mills is significantly higher than in the system used at present.

#### EXAMPLE

In the examples below are compared the steam values, the net electric power and the overall electrical efficiency of a traditional soda recovery boiler and two soda recovery boiler-superheating boiler combinations according to the invention, operating in a pulp mill, in which

- the black liquor flow is 18,5 DS/s
- the bled steam (12bar) demand is 15,4 kg/s and
- the low pressure steam (4,5 bar) demand is 49,6 kg/s

Example case I: A traditional soda recovery boiler which together with a bark-fired boiler produces high pressure steam for turbines, from which further bled steam and low pressure steam for the sulphate pulp process is obtained.

In addition to the high pressure and bleeder turbine, electric power is also generated by a condensing turbine. The values of the produced high pressure steam are: 480 °C, 85 bar.

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Example case II: A soda recovery boiler and a super heating boiler which burns oil obtained from a hydrogenation reactor. The steam is already partially superheated in the soda recovery boiler, but the final superheating is, however, effected in the superheating boiler. A bark-fired boiler additionally produces high pressure steam. The turbine plant does not include a condensing turbine. The oil consumption of the lime sludge reburning kiln is substantially met by the oil and gas obtained from the hydrogenation reactor.

10 The values of the produced high pressure steam are: 540 °C, 100 bar.

Example case III: A soda recovery boiler and a superheating boiler which uses the main part of the oil from the hydrogenation reactor. A condensing turbine is needed. Possible surplus hydrogenation oil is used together with the gas from the hydrogenation in the lime reburning kiln. The values of the produced high pressure steam are: 540 °C, 100 bar:

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The results are shown in the table below. In example case II, the demand of purchased oil for the lime reburning kiln is dispensed with to such an extent that some gas from the hydrogenation will be left over. In example case III, the electric power production has increased considerably and the overall electrical efficiency has risen from 0,239 to 0,257. Additionally, in example case III, the demand of purchased oil for the lime reburning kiln has decreased.

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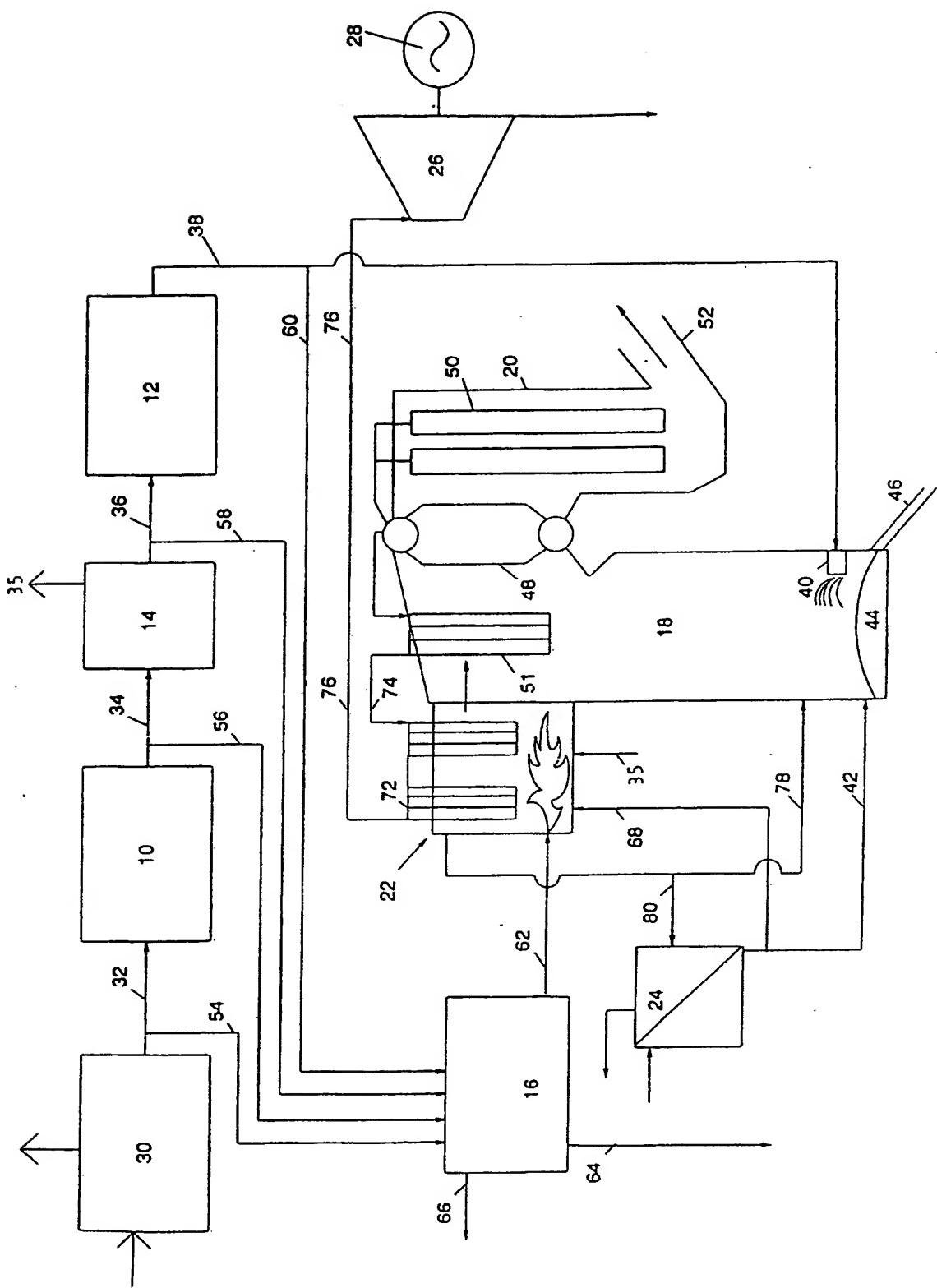
		CASE I	CASE II	CASE III
5	NET ELECTRIC POWER	42.2 MW	42.4MW	45.4 MW
10	STEAM PRODUCED IN SODA RECOVERY BOILER	480 °C /85 bar	420 °C /100 bar	352 °C /100 bar
15	HIGH PRESSURE STEAM VALUES	480 °C /85 bar	540 °C /100 bar	540 °C 100 bar
20	HIGH PRESSURE STEAM QUANTITY	77.2 kg/s	67.6 kg/s	70.7 kg/s
	OVERALL ELECTRICAL EFFICIENCY ( $P_{net} / \phi_{proc}$ )	0.239	0.241	0.257
25	PURCHASED OIL DEMAND FOR LIME REBURNING KILN	18.2 MW	0 MW; surplus of gas from hydrogenation reactor	15.5 MW

The invention is not intended to be limited to the embodiment illustrated and described above but can be modified and varied within the scope and spirit of the 30 invention as defined by the following claims.

## CLAIMS

1. Method of recovering energy from waste liquors from pulp processes, in which method waste liquor is burned in a waste liquor recovery boiler and heat is recovered from the resulting flue gases by producing saturated and/or partially superheated steam,  
characterized in that
  - at least a portion of the waste liquor is treated before it is conveyed to the recovery boiler by a pressure heating process, in order to form a gaseous fuel containing organic components, and/or by a pressurized liquid-phase process in order to form a fraction containing an oleaginous fuel and a fraction containing inorganic components;
  - the waste liquor from the pressure heating process and/or the fraction containing inorganic components formed by said pressurized liquid-phase process are burned in the recovery boiler, and
  - the gas formed during said pressure heating process and/or the fraction containing an oleaginous fuel formed by said pressurized liquid-phase process are burned in the superheating boiler, in which the steam produced in the recovery boiler is superheated.
2. Method according to claim 1, characterized in that 10 - 35 % of the waste liquor is fractionated by a hydrogenation process by means of a high pressure and temperature under reducing conditions, in the presence of e.g. hydrogen or carbon monoxide.
3. Method according to claim 2, characterized in that waste liquor having a dry solids content of 15 - 80 %, preferably 30 - 50 % is supplied to the hydrogenation process.
4. Method according to claim 1, characterized in that the waste liquor is pressure heated in order to release about

- 1 - 3 % weight-% of the dry solids contained therein as a gas containing dimethylsulfide and burning said gas in the superheating boiler.
- 5    5. Method according to claim 1, characterized in that the waste liquor is pressure heated and the gas released thereby converted to give methane and hydrogen sulfide.
- 10    6. Method according to claim 5, characterized in that the methane is burnt in the superheating boiler.
- 15    7. Method according to claim 1, characterized in that superheated steam of > 100 bar and > 520 °C is produced in the superheating boiler.
- 20    8. Method according to claim 1, characterized in that partially superheated steam of < 350 °C, which is finally superheated in the superheating boiler, is produced in the recovery boiler.
- 25    9. Method according to claim 1, characterized in that the superheating boiler is pressurized.
- 30    10. Method according to claim 1, characterized in that the flue gases from the superheating boiler are combined with the flue gases from the recovery boiler.
- 35    11. Method according to claim 1, characterized in that the flue gases from the superheating boiler are used to preheat the air which is to be supplied to the recovery boiler.
12. Method according to claim 1, characterized in that the flue gases from the superheating boiler are led to the lower part of the recovery boiler.



# INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 92/00092

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC  
**IPC5: D 21 C 11/12**

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
IPC5	D 21 C

Documentation Searched other than Minimum Documentation  
 to the Extent that such Documents are Included in Fields Searched<sup>8</sup>

SE,DK,FI,NO classes as above

## III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US, A, 2606103 (A.L. HAMM) 5 August 1952, see column 5, line 6 - line 10; column 6, line 12 - line 39 --	1-12
Y	WO, A1, 8001490 (BATTELLE MEMORIAL INSTITUTE) 24 July 1980, see page 5, line 32 - line 35 --	1-3,7- 12
Y	US, A, 4135968 (GERRIT G. DEHAAS) 23 January 1979, see column 3, line 11 - line 53 -- -----	1,4-6,7- 12

\* Special categories of cited documents:<sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

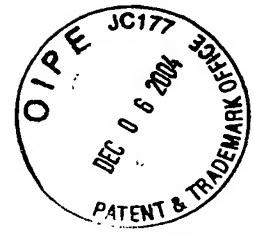
## IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
8th July 1992	1992-07-14
International Searching Authority	Signature of Authorized Officer <i>Marianne Bratsberg</i> Marianne Bratsberg

Form PCT/ISA/210 (second sheet) (January 1985)

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ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 92/00092

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the Swedish Patent Office EDP file on **29/05/92**.  
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 2606103	52-08-05	NONE		
WO-A1- 8001490	80-07-24	EP-A-B-	0022841	81-01-28
US-A- 4135968	79-01-23	US-A-	4338158	82-07-06